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Study of the Crystallization Behavior of Poly(vinylidene fluoride) from the Melt under the Effect of an Electric Field

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ABSTRACT: Fourier transform infrared spectroscopy in the 400–1000-cm^{-1} range was used to study the crystallization behavior of poly(vinylidene fluoride) from the melt in the presence of a weak electric field (0.07 MV/cm). Unlike the usual zero-field case where the α phase is obtained, we found that our samples contain chain conformations which mainly exist in trans sequences usually associated with either the β or γ phases. The relative amount of the α phase to the other phases, as expected, is strongly dependent on the degree of supercooling, the electric field strength, and the time that the poly(vinylidene fluoride) melt is exposed to the electric field.

Introduction

Poly(vinylidene fluoride) (PVF$_2$), because of its unusual piezoelectric properties, is a fascinating polymer to study. Several crystalline phases, α, β, γ, δ, and others, are known to exist in this polymer. The piezoelectricity is principally associated with the β phase. The connection between the crystalline structure and the resultant electrical properties has led to a number of studies in which attempts have been made to prepare different phases by altering thermal history,[1] mechanical deformation,[2] γ irradiation,[3] or pressure,[4] and by the application of a strong electric field.[5-8] Our recent studies have shown that the solid–solid phase transformation from the helical α phase to one containing trans sequences, i.e., either the β or γ phase, can occur with relative ease at high temperatures by applying a moderately strong electric field.[9] We have concluded that phase transformations of this type are strongly affected by the increase in chain mobility at higher temperatures and the decrease in free energy which results from aligning individual dipoles in the electric field.

The process of altering the relative volume fraction of individual crystalline phases by the application of an electric field at controlled temperatures is one method, commonly referred to as poling, to enhance the piezoelectric behavior of PVF$_2$. Although this procedure is a commonly used one, a question often arises as to whether there is a more efficient way to affect the crystalline nature of PVF$_2$. It has been established that the deformation of polymers, rubber for example, to a more extended conformation or a state of greater order can lead to enhanced nucleation and crystallization.[10] We feel that a somewhat analogous experiment is to apply an electric field to PVF$_2$ melt to enhance the relative segmental orientation. Under normal circumstances, for PVF$_2$ crystallized isothermally from the melt at a high degree of supercooling, the α crystalline phase has been found to be the dominant one, with the possibility of a second phase present of the γ form.[11-13] X-ray diffraction studies have shown the conformation of the γ phase to be intermediate between the TGTG′ of the α structure and fully trans β structure, with a T3GT3G′ conformation.[14,15] In the present study, we found that the crystallization process from the melt can be significantly altered by a relatively weak field (0.07 MV/cm) applied to PVF$_2$ in the molten state. Instead of the α phase usually obtained under similar experimental conditions, the PVF$_2$ crystals prepared in this way can contain significant amounts of β or γ forms. Preliminary results of our study are summarized in this paper.

Experimental Section

The PVF$_2$ film (24 μm thick) used in our study was obtained from Kureha Chemical Corp. Gold-palladium electrodes were deposited on the surface of two smooth potassium bromide disks. The electrodes are thick enough to conduct electricity yet still thin enough to transmit infrared radiation. With the PVF$_2$ film between the disks, the distance between the two electrodes was adjusted by using appropriate poly(tetrafluoroethylene) spacers. A high-voltage power supply capable of providing 2500 V was used. The entire experiment was carried out in two isothermal vacuum ovens; one was kept at 215–220 °C, and the second was kept at the desired crystallization temperature, which varied from 100–175 °C. The PVF$_2$ film was kept in the first oven for at least 15 min to obtain the molten state. An electric field of 0.07 MV/cm was then applied for 15 min. The entire assembly was then transferred to the second vacuum oven in order for the PVF$_2$ to crystallize isothermally with the field on continuously. We found that field values stronger than 0.07 MV/cm were impossible to attain due to sample discharging. It was necessary to use a high-value resistor in series with the electrodes to prevent a large current from flowing across the molten PVF$_2$ sample assembly. Each sample was then allowed to crystallize for 3–4 h in the second oven; the samples were then cooled to room temperature for spectroscopic analysis.

Infrared spectra were obtained with a Nicolet Fourier transform infrared spectrometer. Since we are mainly interested in vibrational bands in the 1000–400-cm^{-1} region (and part of this region has relatively low transmittance), a large number of scans, no less than 200, were needed to obtain infrared spectra of acceptable signal-to-noise ratio. Spectral resolution was maintained at 2 cm^{-1}. Typical infrared spectra obtained for the starting PVF$_2$ film and melt are shown in Figure 1. The spectra obtained for PVF$_2$ samples with different thermal histories are shown in Figure 2. When the PVF$_2$ melt was allowed to crystallize in the presence of an electric field, substantial differences in the infrared spectra existed depending on the crystallization temperature. These spectra are shown in Figure 3.

Results and Discussion

In our laboratory, we primarily use vibrational spectroscopy to determine the relative volume fraction of individual crystalline phases in the PVF$_2$ samples obtained. The principal advantage of vibrational spectroscopy when compared to other physical characterization techniques used for the structural determination of PVF$_2$ is its ability to analyze local conformation, packing, and relative changes in orientation. The vibrational spectra of PVF$_2$ are relatively well understood,[16,17] thus providing a proper basis for microstructural analysis. Bands characteristic of mainly helical or extended sequences have been identified and have been widely used in crystallization studies. But it should be emphasized that vibrational spectra often show localized vibrations and are only characteristic of short-range order. Unless used in conjunction with other

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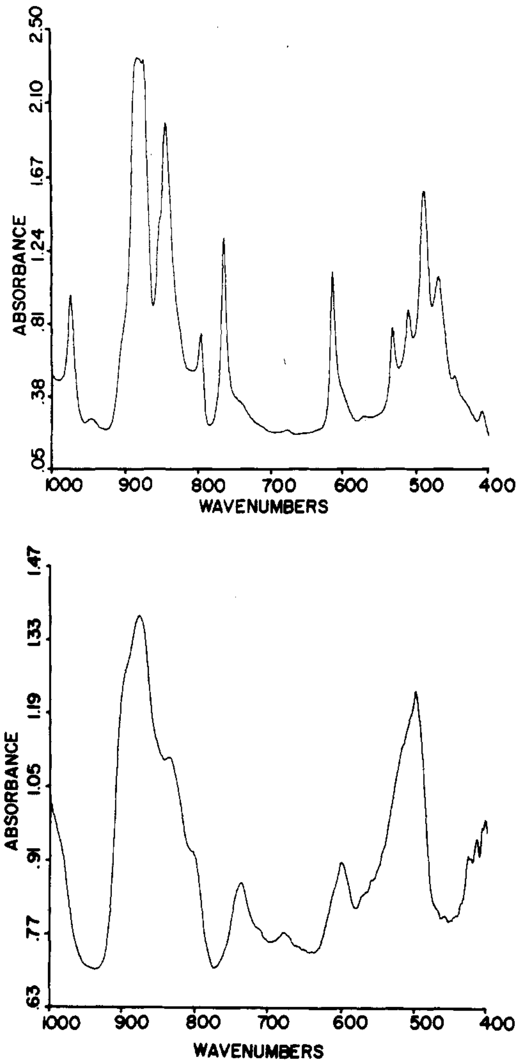

Figure 1. Infrared spectra obtained for poly(vinylidene fluoride) films (24 μm thick), 2-cm^{-1} resolution, 200 scans coadded: (top) as-sent sample; (bottom) sample at 215 °C.

physical techniques such as X-ray diffraction,[18] it is usually difficult to separate features arising from trans sequences in the β or γ forms. Although the 510-cm^{-1} CF_2 bending or the 845-cm^{-1} CH_2 rocking bands have been widely used to characterize the β structure, in light of recent evidence[18] it would be more accurate to assign these bands to be characteristic of trans sequences in either the β or γ forms; instead, the 470-cm^{-1} band is assigned to be characteristic of the β form.

For the PVF_2 film heated to 215 °C for 15 min, all of the crystals were destroyed. The infrared spectrum obtained (Figure 1, bottom) is in complete agreement with previous studies.[17] The α phase is the most common form of PVF_2, normally produced by crystallization from the melt at moderate or high degrees of supercooling.[12,19,20] This conclusion is supported by our spectroscopic data. As can be seen in Figure 2, the infrared spectrum obtained for PVF_2 film crystallized at 145 °C has many features associated with the α phases, with virtually no characteristic features of the β or γ forms present. But a considerably different spectrum was obtained for the sample crystallized at 170 °C. In that case, all the bands associated with the α phase diminished considerably in intensity. Instead, the 815, 776, 510, and 430 cm^{-1} bands gained a considerable amount of intensity relative to others. These bands are all assignable to the γ phase.[11,16] Furthermore, when the sample crystallized at 145 °C was annealed at

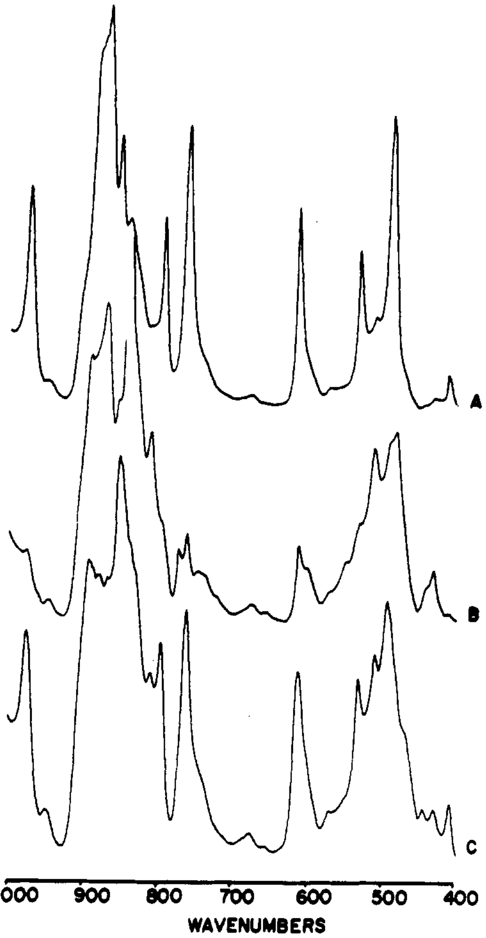

Figure 2. Infrared spectra of poly(vinylidene fluoride) films with different thermal histories, 2-cm^{-1} resolution, 200 scans coadded: (a) crystallized at 145 °C from melt; (b) crystallized at 170 °C from melt; (c) film crystallized at 145 °C and then annealed at 170 °C.

170 °C for 24 h, all the features associated with the γ phase also gained considerably in intensity. Therefore, we can conclude that thermal annealing at sufficiently high temperatures also enhances the amount of the γ phase present. These results are consistent with previous studies.[11,13]

As mentioned earlier, somewhat analogous to the strain-induced crystallization process, we expect that the crystallization process from the melt may be perturbed by the presence of an electric field. A series of spectra showing the effects of the applied field are shown in Figure 3. Even at relatively low crystallization temperatures, such as 100, 120, or 145 °C, when a weak field of 0.07 MV/cm was applied, all the γ bands such as the ones at 815, 776, 510, and 430 cm^{-1} appear. All the α-phase bands, such as the ones at 965, 796, and 530 cm^{-1}, diminished significantly in intensity. In our previous studies we demonstrated that a strong field on the order of at least 1 MV/cm is needed to alter PVF_2 chain conformation even at very high temperatures. In should be noted that nucleation and growth processes may be so fast that the experiments carried out at 100 and 120 °C may not represent the true crystallization behavior at those temperatures. However, our present spectroscopic results demonstrate that the application to the melt of an electric field approximately 2 orders of magnitude lower than previously established values has influenced the isothermal crystallization process.

Since the initial studies by Gianotti et al.[12] and Prest and Luca,[11] studies of this solid–solid phase transformation by altering sample thermal history have been carried out by Lovinger[21] and Takahasi and Tadokoro.[15] This mi-

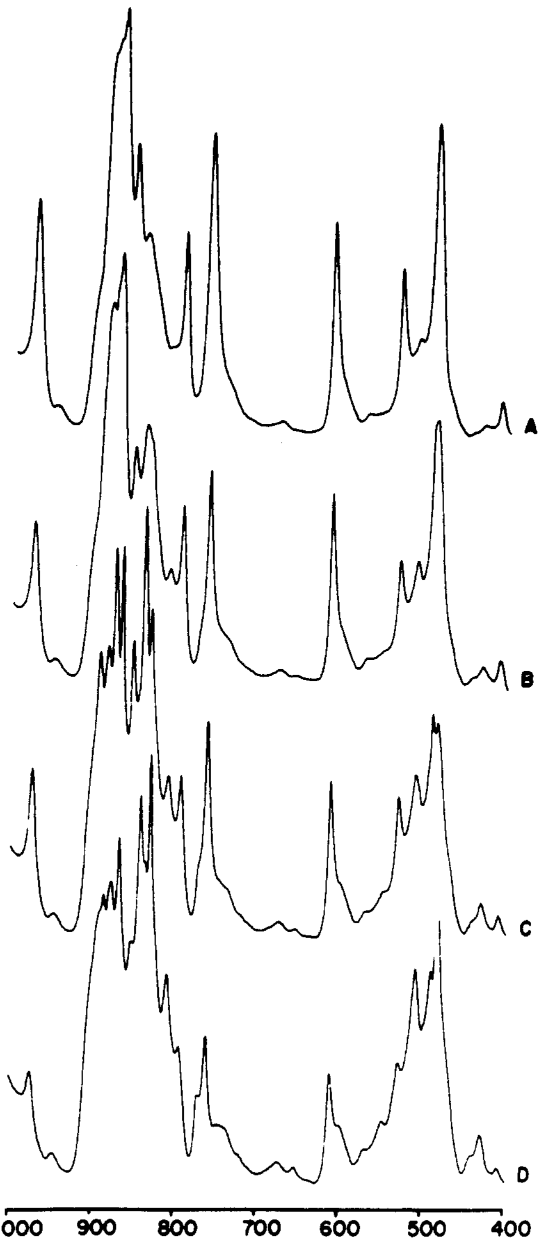

Figure 3. Infrared spectra of poly(vinylidene fluoride) films crystallized in the presence of an electric field, 2-cm^{-1} resolution, 200 scans coadded: (a) crystallized at 145 °C with no field; (b) crystallized at 100 °C with a 0.07 MV/cm field; (c) crystallized at 120 °C with a 0.07 MV/cm field; (d) crystallized at 145 °C with a 0.07 MV/cm field.

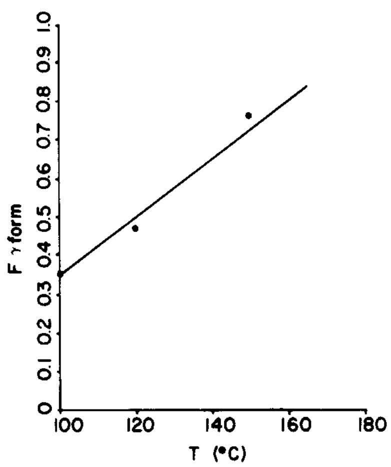

Figure 4. Fraction of the γ form as a function of crystallization temperature for PVF$_2$ samples crystallized for about 200 min in the presence of a 0.07 MV/cm electric field.

crostructural change from the α to the γ phase is interpreted to involve cooperative rotations around skeletal single bonds. Takahashi and Tadokoro proposed that the γ-phase kink bands in conformational changes from TGTG′ to T3GT3G′ are formed by the flip-flop motion between the TGTG′ and TG′TG and the motion from G or G′ to T.[15] In contrast, Lovinger favors the mechanisms involving flexible chain motions consisting of localized seven-bound rotational motions.[21] Both molecular mechanisms proposed would experience substantial nonbonded steric repulsion during the transition to but not necessarily in the γ form. In addition, even though no mechanism has been proposed, many studies have shown that the G conformation in PVF$_2$ can be changed to an entirely trans chain when poled or mechanically deformed. Therefore, for PVF$_2$ chains in a highly mobile state such as the melt, the net effect of the electric field may be to change the conformation of the chains to align the dipoles, allowing the γ phase to crystallize.

We are also interested in the determination of the amount of trans sequence present. This can be accomplished by measuring the relative intensities of the 530- and 510-cm^{-1} bands. As mentioned previously, we take the 510-cm^{-1} band to represent the amount of the γ form present. When the relationship first proposed by Ishida[22] is used, the amount of the γ form determined for our samples obtained as a function of the crystallization temperature is shown in Figure 4. The crystallization kinetics have been analyzed and will be published separately.[23] It is interesting to note that at very low supercoolings, T_c = 175 °C, in the absence of an electric field, the amount of the γ phase obtained is approximately 80%. However, even for samples prepared at a much higher degree of supercooling of T_c = 145 °C, the application of an electric field can contribute significantly to the overall free energy, also allowing approximately 76% of the crystallites to be formed as the γ form. Although several theoretical analyses are currently under way,[23,24] a quantitative interpretation of the crystallization behavior for PVF$_2$ chains in the presence of an electric field is still unavailable. In this paper, we have shown that the application of an electric field can significantly alter the crystallization process of PVF$_2$ melt, causing the γ form to be the dominant one. This observation is interesting from fundamental as well as technological viewpoints and should be incorporated in future theoretical considerations.

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Registry No. PVF$_2$ (homopolymer), 24937-79-9.

References and Notes

(1) Takahashi, Y.; Matsubara, Y.; Tadokoro, H. *Macromolecules* **1982**, *15*, 334.
(2) Matsushige, K.; Nagata, K.; Imada, S.; Takemura, T. *Polymer* **1980**, *21*, 1391.
(3) Kasmynin, B. P.; Gal'Perin, E. L. *Vysokomol. Soedin., Ser. A* **1972**, *A14*, 1603.
(4) Matsushige, K.; Takemura, T. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 921.
(5) Das-Gupta, D. K.; Doughty, K. *J. Appl. Phys.* **1978**, *49*, 4601.
(6) Davis, G. T.; McKinney, J. E.; Broadhurst, M. G.; Roth, S. C. *J. Appl. Phys.* **1978**, *49*, 4998.
(7) Newman, B. A.; Yoon, C. H.; Pae, K. D.; Scheinbeim, J. I. *J. Appl. Phys.* **1979**, *50*, 6095.
(8) Luongo, J. P. *J. Polym. Sci., Polym. Phys. Ed.* **1972**, *10*, 1119.
(9) Hsu, S. L.; Lu, F. J.; Waldman, D. A.; Muthukumar, M. *Macromolecules*, in press.

Macromolecules **1986**, *19*, 329–332 **329**

(10) Wunderlich, B. "Macromolecular Physics"; Academic Press: New York, 1976; Vol. I and II.
(11) Prest, W. M., Jr.; Luca, D. J. *J. Appl. Phys.* **1975**, *46*, 4136.
(12) Gianotti, G.; Capizzi, A.; Zamboni, V. *Chim. Ind. (Milan)* **1973**, *55*, 501.
(13) Lovinger, A. J. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 793.
(14) Weinhold, S.; Litt, M. H.; Lando, J. B. *Macromolecules* **1980**, *13*, 1178.
(15) Takahashi, Y.; Tadokoro, H. *Macromolecules* **1980**, *13*, 1317.
(16) Kobayashi, M.; Tashiro, K.; Tadokoro, H. *Macromolecules* **1975**, *8*, 158.
(17) Cortili, G.; Zerbi, G. *Spectrochim. Acta* **1967**, *23A*, 2216.
(18) Yang, D. Y.; Thomas, E. L. *J. Mater. Sci. Lett.* **1984**, *3*, 929.
(19) Nakamura, S.; Sasaki, T.; Funamoto, J.; Matsuzuki, K. *Makromol. Chem.* **1975**, *176*, 3471.
(20) Mancarella, C.; Martuscelli, E. *Polymer* **1977**, *18*, 1240.
(21) Lovinger, A. J. *J. Appl. Phys.* **1981**, *52*, 5934.
(22) Ishida, Y.; Watanabe, M.; Yamafuji, K. *Kolloid Z. Z. Polym.* **1964**, *200*, 48.
(23) Stein, R. S.; Muthukumar, M.; Hsu, S. L., to be published.
(24) Barker, R. E., Jr.; Campbell, K. W.; Huang, C. C. *Bull. Am. Phys. Soc.* **1985**, *30* (3), 491.

Investigation of the Curing of Phenolic Resins by ^{2}H NMR Spectroscopy

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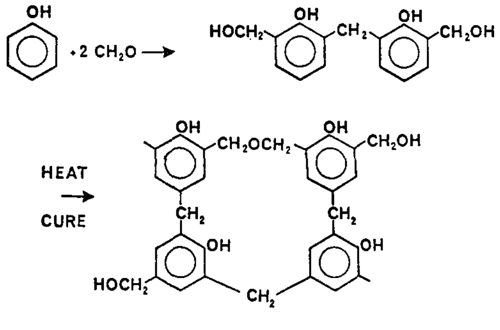
ABSTRACT: The curing of specifically deuterated phenol/formaldehyde resins has been studied by ^{2}H quadrupole echo NMR. The ^{2}H NMR spectra of the cured resins are characterized by quadrupole patterns with a rigid limit quadrupole splitting, indicating that the resin is rigid on a time scale of 10^5 Hz. The ^{2}H NMR spin–lattice relaxation times, which reflect motional processes in the materials, show a rapid increase with curing time followed by a leveling off. This increase in T_1 parallels the increase in the number of cross-links, as reflected by the increase in the methylene/methylol ratio, detected by ^{13}C solid-state CP MAS NMR. Resins prepared with deuterated formaldehyde also show the presence of C^2H_3 groups when they are cured at 120 °C for 4 h or more, indicating that degradation of the resin is occurring.

Introduction

The reaction of phenol with formaldehyde to give phenolic resins is of significant commercial importance. The cured resin, commonly called Bakelite, is highly cross-linked, giving it considerable mechanical strength and good ablative properties.

If the polymerization reaction is performed under basic conditions a resol-type product (prepolymer) is formed. Curing of the resol gives a polymer with free methylol groups but cross-linked with methylene bridges and benzyl ether linkages (Scheme I). The solid-state curing of the resin has been studied extensively by ^{13}C solid-state CP MAS NMR.[1-4] The combined[5] use of cross polarization (CP),[6] high-power decoupling, and magic angle spinning (MAS)[7] has enabled high-resolution ^{13}C spectra of the solid polymers to be obtained. The curing process is characterized by a decrease in the intensity of the resonance attributed to free methylols and benzyl ether linkages, both of which are also detected by IR.[8] As this resonance decreases, there is a concomitant increase in the intensity of the peak assigned to bridging methylene groups. This variation in the methylene/methylol peak area has been used to monitor the curing process of phenol/formaldehyde resins at a variety of temperatures.[2,3]

Scheme I



In the present study, the curing process has been studied by ^{2}H NMR. Since deuterium has a spin $I = 1$ the deuterium nucleus has a quadrupole moment, which arises from the nonspherical charge distribution inside the nucleus. In the solid state, the ^{2}H NMR spectrum is completely dominated by the interaction of this quadrupole moment with the electric field gradient generated by the C–^{2}H bonding electrons. For a single crystal containing only one type of deuteron the ^{2}H NMR spectrum will show two lines, for the two allowed transitions, with a spacing ($\Delta\nu$) equal to the strength of the quadrupole interaction (the quadrupole coupling constant) modulated by the orientation of the C–^{2}H bond with respect to the external magnetic field. The magnitude of this quadrupole interaction is shown in eq 1, where θ is the angle between the C–^{2}H bond vector and the magnetic field and e^2qQ/h is the quadrupole coupling constant.

$$\Delta\nu = \frac{3}{4}\frac{e^2qQ}{h}(3\cos^2\theta - 1) \qquad (1)$$

However, since the cured phenolic resin is amorphous, all possible orientations of the C–^{2}H bond can occur. The resulting spectrum is a Pake doublet with the singularities (the $\theta = 90°$ orientations and indicated by the arrows in Figure 2B) separated by the quadrupole splitting, $\Delta\nu_Q$.

$$\Delta\nu_Q = \frac{3}{4}\frac{e^2qQ}{h} \qquad (2)$$

For aliphatic deuterons the coupling constant generally takes a value of ≈167 kHz while aromatic deuterons have a value of ≈176 kHz. This leads to quadrupole splittings of ≈125 kHz for rigid aliphatic deuterons and ≈132 kHz

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